

DIRECTIONAL SOLIDIFICATION AND MAGNETIC PROPERTIES OF SOME B₁-Mn ALLOYS

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in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
AMIT BHADURI

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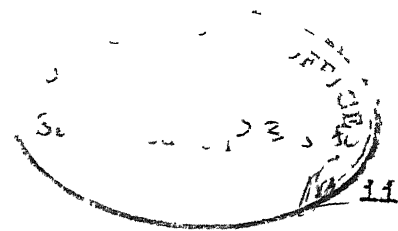
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CERTIFICATE

This is to certify that the work entitled
'Directional Solidification and Magnetic Properties of
Some Bi-Mn Alloys' has been carried out by Amit Bhaduri
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ABSTRACT

Directional solidification of Bi-.5,2,8,12,13,15,30 and 35 wt % Mn alloys have been performed. Alloys were first induction melted for making ingots and then directionally solidified by using Stockbarger method. The cast and directionally solidified microstructures have been recorded. In the Bi-Mn alloy the microstructure contains flakes of BiMn (H.C.P.) phase, embedded in the matrix of Bi (Rhombohedral) below 21 wt % Mn, and embedded in the matrix of Mn (B.C.C.). The Bi-Mn alloys exhibit ferromagnetic properties although the constituent elements Bi and Mn are non-magnetic in nature. The directionally solidified alloys show anisotropic magnetic properties with respect to the direction of solidification. Some magnetic properties of these alloys were measured and compared to those of commercially used permanent magnets.

CHAPTER 1

INTRODUCTION

During the solidification of an alloy of eutectic composition, solidification gets initiated at the mold walls and the resulting microstructure consists of small packets of eutectic structure randomly oriented with respect to one another. However if solidification is controlled and made to occur in one direction, then the microstructure will consist of these same packets of eutectic structure i.e. phase particles oriented parallel to one another and aligned along the direction of heat extraction. Such unidirectional solidification can be obtained by slowly withdrawing a furnace from a stationary molten charge chilled at one end by a copper block. This creates a substantially uniaxial heat flow and a planar solid-liquid interface normal to the direction of furnace movement. This specialized method of casting, mentioned above, is known as "Directional solidification", which makes superior alloys with anisotropic properties.

Two dominant micromorphologies have been produced using this above technique:

- (i) That of substantially parallel alternating lamellae of each phase and
- (ii) Globules or long parallel rods of one phase embedded in a continuous matrix of the other phase.

A desired columnar structure can be produced by maintaining sufficiently high thermal gradient ahead of the solid-liquid interface, together with a high growth rate, and extracting the heat unidirectionally from the melt. Increasing the growth rate produces increasingly finer microstructures and thereby improves the mechanical and physical properties.

In directionally solidified alloys the grain boundaries are oriented predominantly parallel to the direction of solidification. Such alloys have reduced tendency for intercrystalline fracture along grain boundaries at high temperatures arising from excessive creep, creep rupture and thermal fatigue. Fracture¹ in ^{such} alloys is found to take place by shear failure of the columnar grain structure or due to fracture of the aligned rods of the second phase.

Following are the attractive properties of directionally solidified structures²:

- (a) Permanent magnets with oriented structures
- (b) High strength
- (c) Superior thermal shock properties
- (d) Longer cyclic strain life
- (e) Longer creep life
- (f) Better intermediate temperature ductility
- (g) Oxidation and hot corrosion resistance

The above properties result from³:

- (i) Improved distribution of second phase particles
- (ii) Preferred crystallographic texture
- (iii) Reduced microporosity
- (iv) The distribution of microsegregation in the columnar grain material is more uniform than that in the conventionally solidified material.

From the above points, it is clear that directionally solidified products are relatively free from casting defects. The disadvantages^{are} (i) higher cost, (ii) difficult processing methods, and (iii) higher creep rates at intermediate temperatures⁴.

The directionally solidified alloys are used in at least 3 different areas:

- (a) For many room temperature applications requiring improved properties particularly resistance to fracture, where the ingots could be worked subsequent to directional solidification.
- (b) In production of high temperature turbine blades.
- (c) To produce hard magnetic materials, where directional magnetic properties are desired.

Among the processing techniques, the well established power down process is now being replaced by high rate solidification technique⁵. This method offers higher temperature gradients, increased solidification rates, and greater operational simplicity.

Unidirectional heat transfer can also be accomplished by other specialized methods of liquid metal cooling, discussed later.

Producing directionally solidified microstructures in the binary Bi-Mn system is reported here. The Bi-Mn alloys are known to display interesting ferromagnetic properties though both Bi (rhombohedral) and Mn (B.C.C.) are non-magnetic. In these alloys this property is supposed to be arising due to the ferromagnetic BiMn (H.C.P.) phase⁶. In a binary alloy the dispersion and distribution of the BiMn phase can be effectively controlled by directional solidification to produce ingots with different magnetic properties parallel to the longitudinal and transverse directions of solidification. These alloys are known to be used as permanent magnets and memory materials in computers⁶.

This work has been undertaken in continuation of an earlier work on unidirectional solidification of Bi-Mn system⁷ as an extensive new area development in the Department of Metallurgy of I.I.T. Kanpur.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Conditions for Directional Solidification:

There are 2 rules that must be followed to prevent equiaxed grain nucleation in the liquid. The melt temperature must be maintained above the liquidus and effective nucleating substrates must be removed from the melt.

Directional solidification of multicomponent eutectics is satisfactorily accomplished by maintaining a planar growth front and by fulfilling the following conditions⁵ at the solid-liquid interface:

- (a) Unidirectional heat transfer from the melt.
- (b) No nucleation ahead of the interface.
- (c) $\frac{G_L}{R} > 0$, where G_L is the temperature gradient in the liquid at the solidifying interface and R is the solidification rate.
- (d) No convection current within the melt and no thermal fluctuations at the interface.

2.2 Unidirectional Heat Flow:

Unidirectional solidification is such that most heat flows unidirectionally through one plane i.e. the bottom chill face via conduction. Therefore,

- (a) The chill must have high thermal conductivity to conduct the sensible heat out of the system. This may be enhanced by water cooling.
- (b) The surface of chill must be cleaned before each casting run, so that resistance to heat flow by oxide layers is minimized.
- (c) Mold (i.e. crucible) should be securely clamped to the chill plate.

There may also be other types of heat transfer. Convective heat transfer for example may result in striations interrupting the continuity of the columnar grains from directional solidification and thus weakening the structure. Convection arises⁵ due to thermal and concentration gradients together with gravitational forces.

Thus, for good directional solidification, a perpendicular arrangement of crucible containing the melt, with a continuously rising temperature to the top of the crucible is a necessary requirement.

Convection currents may also be kept to a minimum, by not resorting to induction methods of heating.

In radiative type of heat transfer, the factors affecting the rate of cooling are the initial temperature and size of the grains⁸. Other physical conditions such as

emissivity of the alloys etc. are fixed parameters. In fact only a small part of the heat is lost by radiation.

2.3 Characteristics of S-L(Solid-Liquid) Interface and Solidification:

The morphology of a S-L interface results from interaction between certain phase-diagram characteristics and the freezing parameters; these are the freezing rate V , the temperature gradient in the liquid at the interface G , the diffusion coefficient of solute in the liquid D , and the freezing range (F.R.) of the alloy in question. This interaction has the form $(G/V - F.R./D)^9$.

When

(a) $\frac{G}{V} - \frac{F.R.}{D} > 0$ - Smooth S-L interface except grooves out the intersection of grain boundaries and interfacial plane, which is termed plane front growth.

(b) $\frac{G}{V} - \frac{F.R.}{D} < 0$ - Depression (called node) forms at the S-L interface where solute segregates.

(c) $\frac{G}{V} - \frac{F.R.}{D} = 0$ - No change in S-L interface structure.

The interface can broadly be defined as the boundary between the liquid and the solid. It is normally described as

'smooth' when the boundary is discrete and 'rough' when the transition extends over a number of atomic layers.

The growth rate of a crystal depends on the difference between the rate at which atoms add themselves to the interface and the rate at which they leave ~~the~~ interface. The interface advance can be attributed essentially to the two principal forms of interfaces which are¹⁰

- (a) Atomically rough and non-crystallographic in character and
- (b) Smooth and crystallographically faceted.

Thermal gradient and growth rate must be controlled to maintain a stable plane front interface, and fluctuations in growth rate lead to compositional (as well as structural) variations along the growth direction. In polyphase alloys, complication arises from the fact that solute must diffuse transverse to the growing interface as well as in the growth direction. Some metals show preferred orientation under directional solidification conditions, e.g., for cubic metals³ the most favourable direction of growth is always $\langle 100 \rangle$.

Eutectic alloys generally show a relationship between undercooling (ΔT), growth rate (R) and interlamellar spacing (λ) which is given by³:

$$\Delta T = A R \lambda + \frac{B}{\lambda} \quad (1)$$

where A and B are constants depending on a particular alloy system. Maximization of equation (1) $(\frac{\delta \Delta T}{\delta \lambda} = 0)$ gives:

$$\lambda^2 R = \frac{B}{A} = \text{constant} \quad (2)$$

which is found to be true in many eutectic systems.

that
Under the assumption \angle convection, lateral composition gradients etc. are negligible for plane front solidification, the solid-liquid interface is stable when,

(1) For single phase alloys³:

$$\frac{G_L}{R} \geq - \frac{m_L C_0 (1-K)}{K D_L} \quad (3)$$

and

(2) For a two phase eutectic alloy³:

$$\frac{G_L}{R} \geq - \frac{m_L (C_E - C_0)}{D_L} \quad (4)$$

where G_L = temperature gradient in the liquid at the liquid-solid interface

R = solidification rate

m_L = slope of the liquidus line

C_0 = average composition of the alloy

K = equilibrium partition coefficient i.e.

$$K = \frac{\text{solute concentration in the solid at temperature } T}{\text{solute concentration in the liquid at the same temperature}}$$

$$= \frac{C_S}{C_L}$$

D_L = diffusion coefficient of solute in the liquid

C_E = eutectic composition

CHAPTER 3

DIRECTIONAL SOLIDIFICATION METHODS

There are several techniques⁹ for controlling heat transfer to provide unidirectional solidification.

(1) The mold is suitably insulated so that after the molten metal is cast; most heat flow takes place through some bottom chill face. Since liquid superheat is rapidly lost via conduction to the chill face, it must be replenished as growth continues, and external heat is added to the system through it's sides from the exothermic compound comprising the mold. This method is the simplest and cheapest of all practical techniques for ensuring predominantly unidirectional heat flow.

It is essential that the mold be in a vertical position so that S/L interface advances in a predominantly horizontal plane, which reduces the convective fluid motion and radial heat transfer usually associated with a vertical S/L interface. As the melt superheat gradually dissipates, the temperature gradient in the liquid gradually decreases until nucleation takes place and columnar growth ceases.

A major problem with this casting method is that both solidification rate and temperature gradient decrease with distance from the chill. Thus mechanical properties may get degraded due to cell or dendrite formation.

(2) Controlling Heat Transfer Rate by an External Power Source:

There are several methods⁹ by which controlled columnar growth can be obtained.

(a) "Power down" growth control method⁵ in which heat transfer rate is controlled by gradually lowering the power in the furnace that surrounds a fixed mold. For high melting alloys, this method is generally adopted.

In the power down technique, an open ended mold is attached to a water cooled copper chill, and placed in a two zone induction coil, coupled by a graphite susceptor for heating. The superheated alloy is poured to the hot mold with the induction coils energized above the melting point of the alloy and with an established temperature profile along the axis.

The bottom coil is turned off after holding the alloy for some time for purposes of equilibration and the directional solidification is allowed to proceed in the axial temperature gradient. Since the solid-liquid interface moves away from the chill surface, solidification rate decreases, with structural variations at the top of the ingot.

(b) "High rate solidification" method⁵ (Generally adopted for high melting alloys) in which heat transfer rate is controlled by withdrawing the mold and maintaining the power source in a fixed position.

The high rate solidification is essentially an improvement on the power down method permitting efficient directional heat transfer. Here the crucible attached as before is withdrawn from a single zone induction heating through a radiation baffle, which helps to maintain a uniform temperature within the heated zone by preventing any radiation losses. This method is known to produce a much more refined microstructure.

(c) (1) The "modified Stockbarger⁹ method" (for low melting alloys, this method is separately discussed in Chapter 4) in which heat transfer rate is controlled by moving the heat source (furnace), keeping the mold (crucible) in a fixed position. This method can almost totally eliminate the variable structure disadvantage of the "power down" technique. This technique has the advantage that the thermal environment during freezing remains nearly constant throughout a large portion of freezing cycle. Columnar castings can be solidified almost four times faster with this method than with the power down technique.

(11) "By moving the heat source, keeping the mold in a fixed position" - based on this above mentioned same principle, a new method⁹ of structure control has been developed which involves a stationary mold and a small movable zone heating source. The mold may be rotated during freezing to inhibit natural convection and thus heat transfer from the melt to the solid is decreased.

The temperature gradient in the melt remains positive for a significantly longer time than in a conventional static casting. The consequent result is that the rate of crystal nucleation is decreased and castings can be grown with a much larger proportion of columnar growth.

(3) "Liquid metal cooling" Technique¹¹: Generally adopted for high melting alloys.

In this method a low melting liquid metal with low vapour pressure is used as a heat sink in the liquid state. This method provides a nearly axial heat flow pattern for solidification.

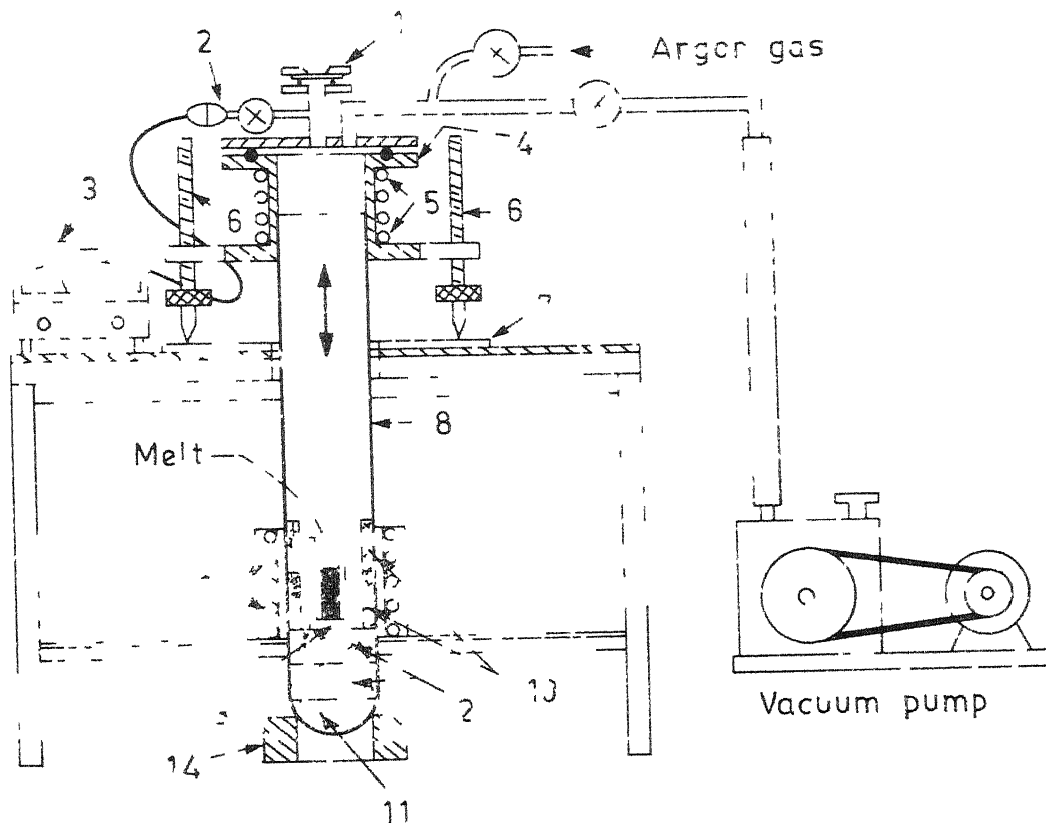
CHAPTER 4

EXPERIMENTAL METHODS FOR ALLOYS UNDER INVESTIGATION

Small ingots (weighing about 60 gms) of different compositions were prepared by vacuum induction melting, (Fig.4-1) by using shots of Bi (99.99%) and finely ground Mn (99.99%): Each alloy was induction melted at least twice using a soaking period of one hour at about 1000°C to ensure homogeneity of composition. The composition of the alloys changed considerably during melting due to sublimation of the constituent elements. The stated compositions were finally obtained from gravimetric analysis performed on as cast ingots. From each alloy cast, samples were taken for microstructural examination and magnetic property measurements.

The remaining portion of ingot was ground and remelted in the experimental set up for directional solidification under inert argon atmosphere. Before directional solidification, the alloy is soaked for a period of about 2 hours at a temperature of 900°C, to avoid any Mn segregation. Directional solidification was performed according to the Stockbarger method (Fig.4-2).

This Stockbarger method (Fig.4-2) essentially consists of an assembly of two furnaces F(I) and F(II) with a baffle plate between the two furnaces. These two furnaces are normally maintained at two different temperatures, with F(I) above the



1	View port	8	Quartz tube
2	Thermocouple vacuum gauge tube	9	Induction coil
3	Vacuum gauge	10	Refractory lining
4	Brass head	11	Refractory base
5	Cooling coil	12	Refractory spacers
6	Levelling screws	13	Susceptor and crucible assembly
7	Base plate	14	Quartz tube support

Fig 4 1 Schematic representation of induction melting unit

melting point and F(II) below the melting point of the alloy. The baffle plate facilitating to create a sharp temperature gradient between the two furnaces.

The whole crucible and chill assembly is enclosed in a quartz tube, through which argon (Ar) is flushed continuously till solidification is complete. After the required temperature gradient is established (Fig.4-3), the furnace assembly is moved upwards leaving crucible-chill assembly stationary and till the crucible containing the alloy reaches the temperature zone maintained below the melting point of alloy. In the experiment performed, the rate of upward motion of the furnace was 8 cm/hour. In this apparatus the crucible assembly is decoupled from the main drive system, making it free from all vibrations. The rate of solidification would be equal to the rate of motion of the furnace assembly.

The directionally solidified small ingots are sectioned transverse and parallel to the growth direction for microstructural examination. The microstructures are shown in Chapter 5. From each of directionally solidified alloys, sample is prepared for magnetic measurements the value of which is recorded in Chapter 5.

Magnetic property measurements were made on specimens

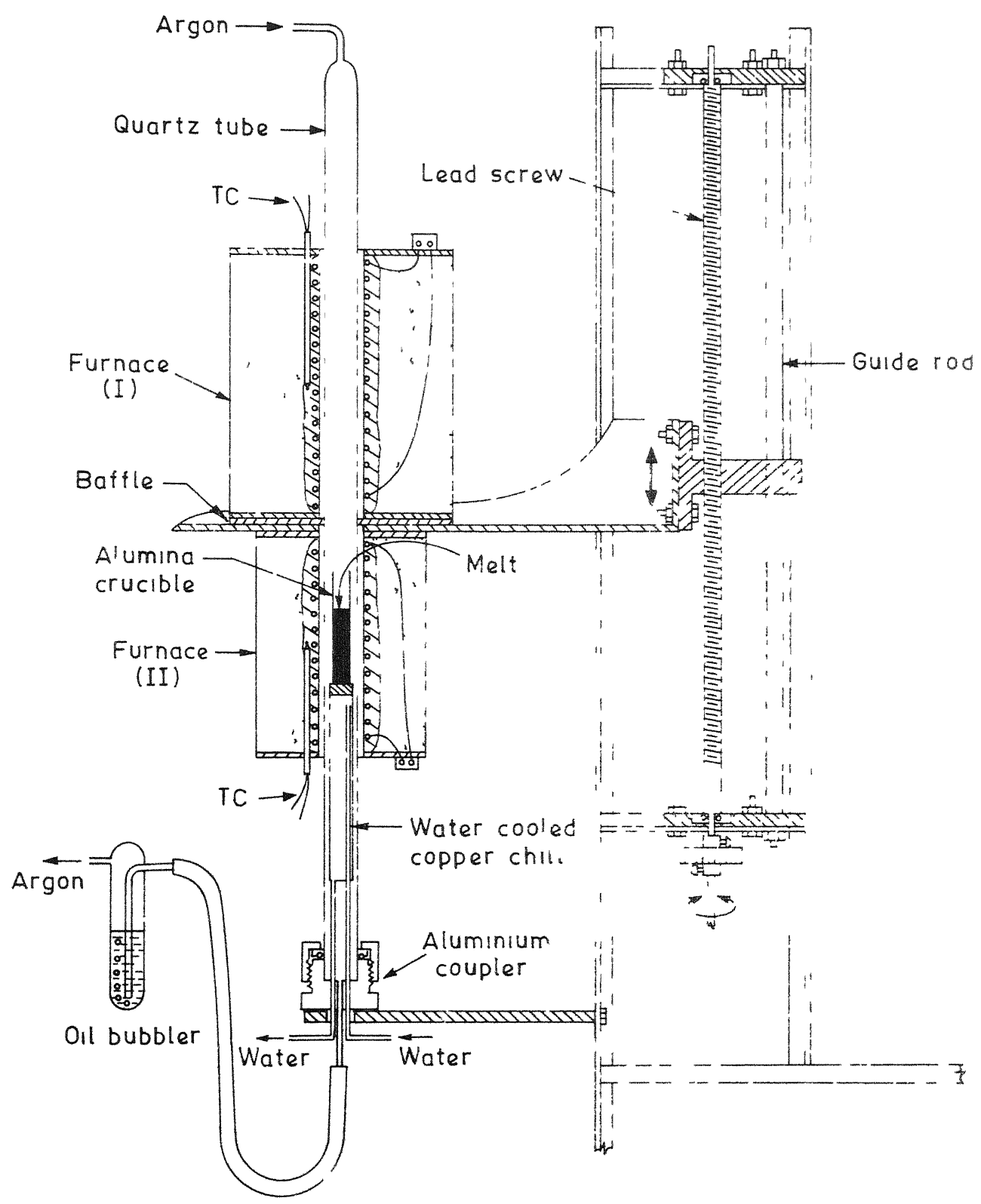


Fig 4 2 Stockbarger apparatus for directional solidification

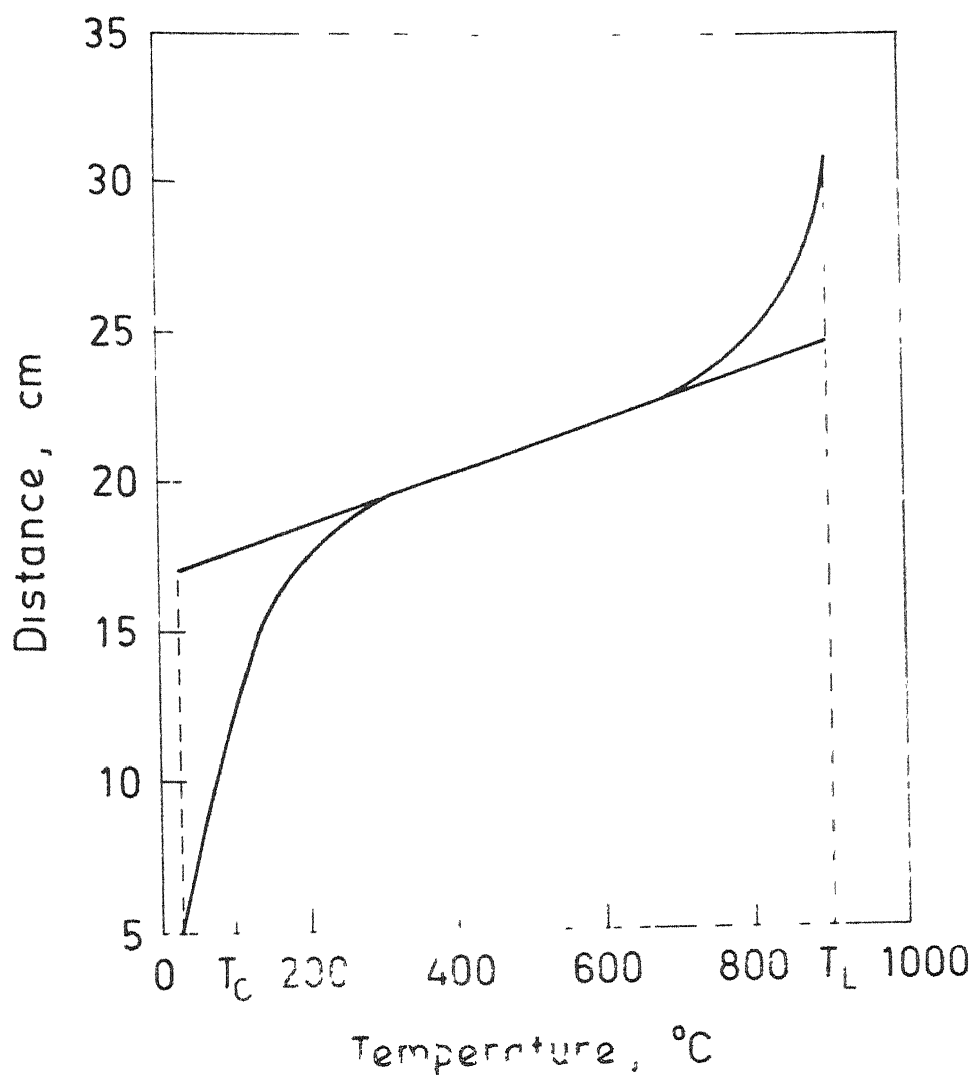


Fig 4 3 Approximate temperature profile within the Stockbarger apparatus
T_L temperature of the liquid = 900 °C
T_C temperature of the chill = 25 °C

of very small dimensions (≤ 5 m.m. in each side), which were prepared from as cast and directionally solidified ingots, in a vibrating sample magnetometer (model 155, Princeton Applied Research Corporation, U.S.A.) (Fig. 4-4). Magnetic measurements for directionally solidified alloys were done along the axis of solidification and perpendicular to the axis of solidification. Magnetic measurements for cast alloys were done along any direction because flakes of ferromagnetic BiMn are oriented randomly in as cast samples. In the directionally solidified alloys these flakes are predominantly oriented parallel to the direction of solidification, thus giving rise to anisotropic magnetic properties.

The vibrating sample magnetometer¹² is an induction instrument in which the output voltage is sinusoidal. The sample is vibrated in a uniform magnetic field in a periodic motion relative to a pickup coil, and the changing flux through the coil generates a voltage which is proportional to the sample magnetic moment. Sample is vibrated with the help of a loudspeaker or an electric motor.

The voltage in the pickup coils from the vibrating sample may be compared to a reference voltage from a permanent magnet or a feedback coil fixed on the sample rod. When a feedback coil is used, the current in this coil can be so adjusted to give a signal in the reference coils which will just balance

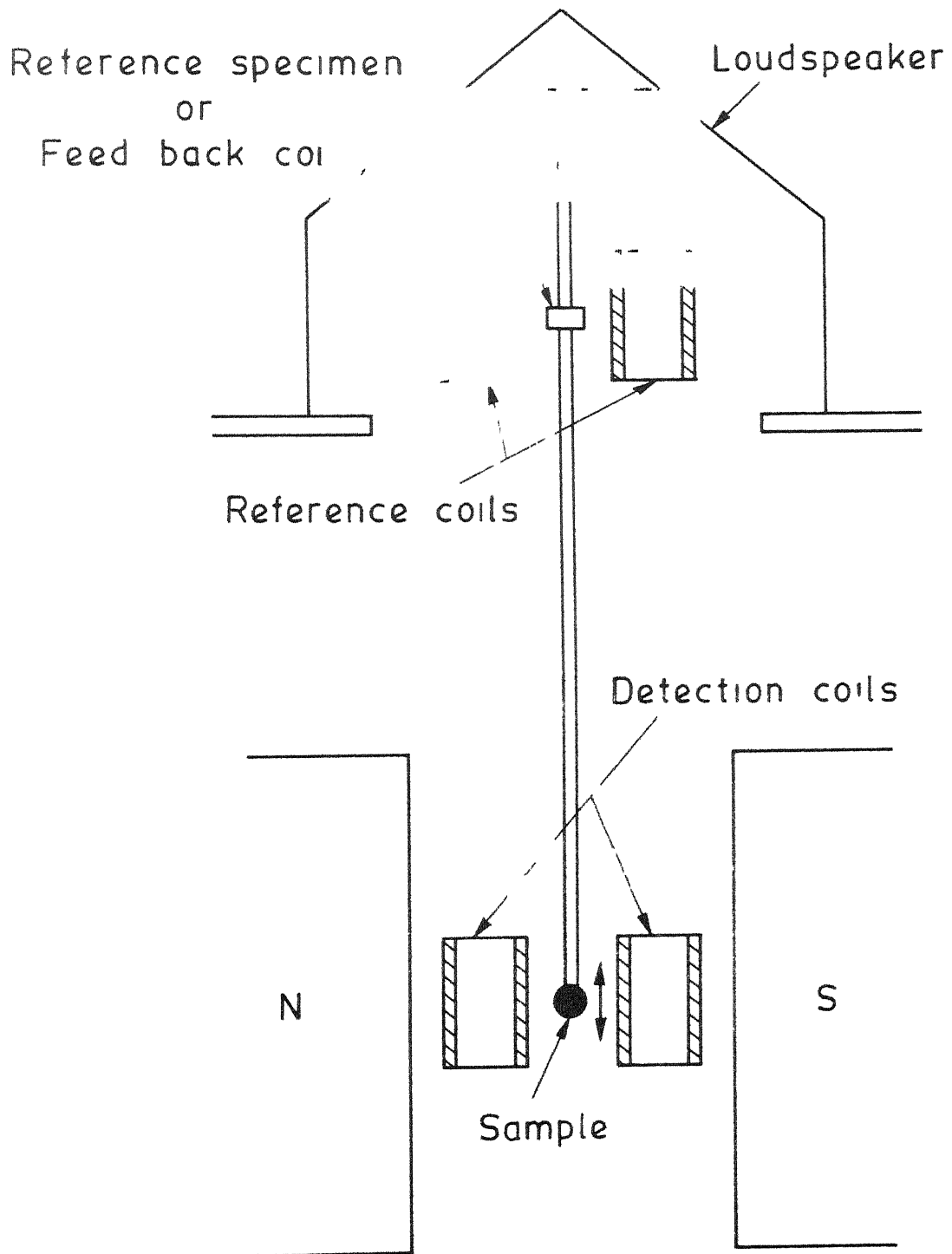


Fig 4 4 Vibrating - sample magnetometer

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out the signal in the pickup or sample coils. Thus, a null measurement system is used. If this is done by an automatic feed back loop (such as the Princeton Applied Research Instrument) then the current in the feed back coil is always proportional to the sample magnetic moment and this current can be recorded*

The following magnetic properties are considered (Fig.4-5):

Saturation Magnetisation (M_S)

Remanent Magnetisation (M_r) and

Coercivity (H_C)

M_S for samples are measured in unit of e.m.u./gm. To convert e.m.u./gm. into unit of K.Gauss, the following relation is used:

(Measured value of M_S in e.m.u./gm.)_{sample} \times (density)_{sample} \times .0122 = the result of this above calculation will give the value of M_S in unit of K.Gauss.

From M_S and H , susceptibility (K) defined as $\left(\frac{M_S}{H}\right)$ and permeability μ . K and μ are related as follows:

$$\mu = 1 + 4\pi K$$

K and μ are calculated.

The results are tabulated in Table I. Some properties of these alloys are compared with a few standard commercially

used ferromagnetic materials in Table II.

* Note: This magnetometer has some limitations, i.e. it records a full B-H loop only for materials which are very strongly ferromagnetic. Since the alloys under investigation do not fully fit into this category of highly ferromagnetic materials, so only M_S , M_R and H_C are recorded separately for each sample.

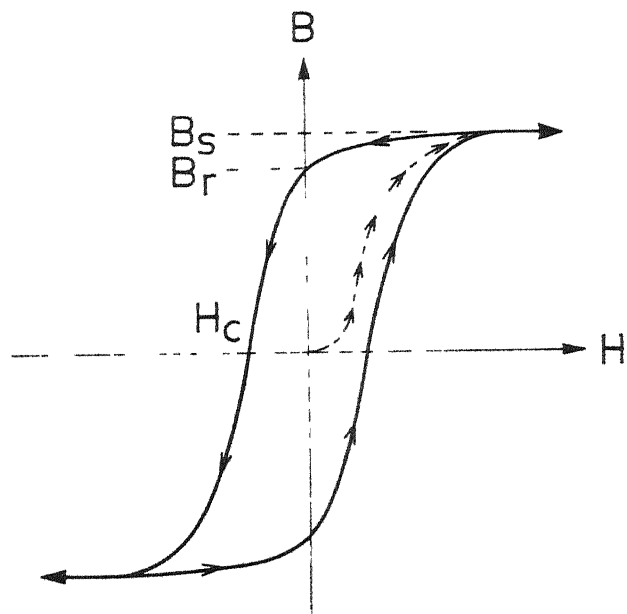


Fig 4 5 B versus H hystereses loop for a ferromagnetic material

CHAPTER 5

RESULTS AND DISCUSSIONS



Figure 5-1. As cast structure of Bi-15 wt% Mn alloy
BiMn flakes are randomly oriented in the
Bi-matrix
Magnification x 100

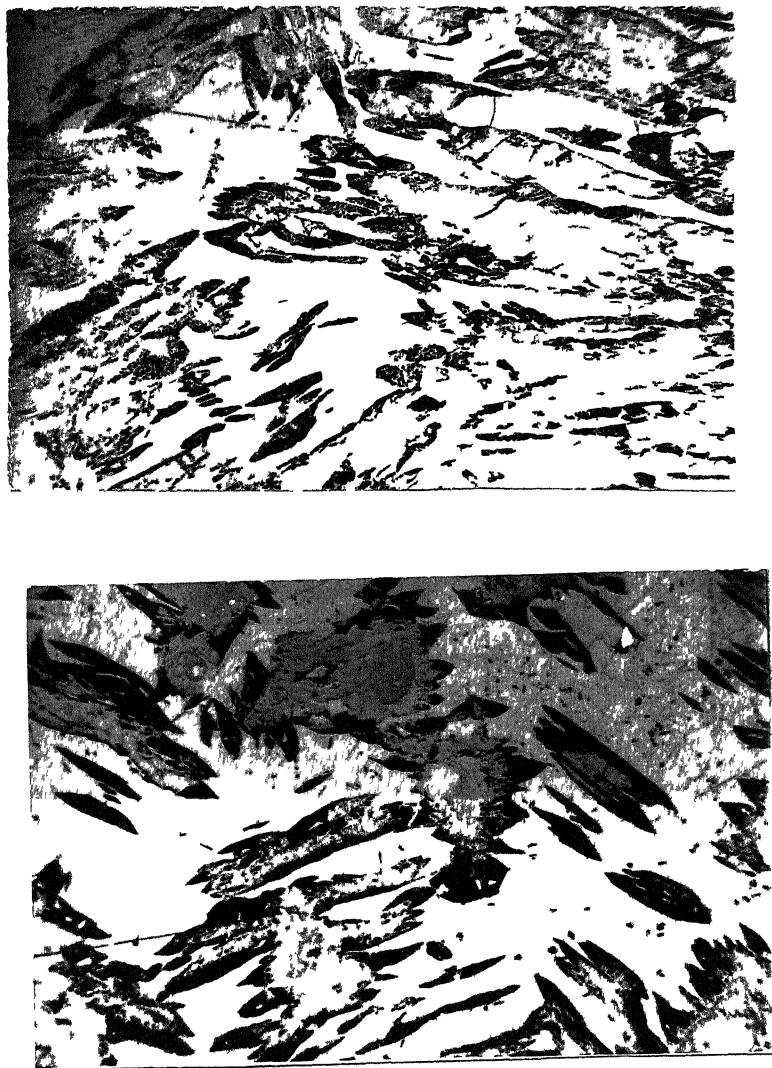


Figure 5.2. Directionally solidified Bi-13 wt% Mn alloy

- (a) Longitudinal section- showing orientation of BiMn flakes parallel to the heat flow direction.
- (b) Transverse section-revealing cross-section of BiMn flakes.

Magnification x 50

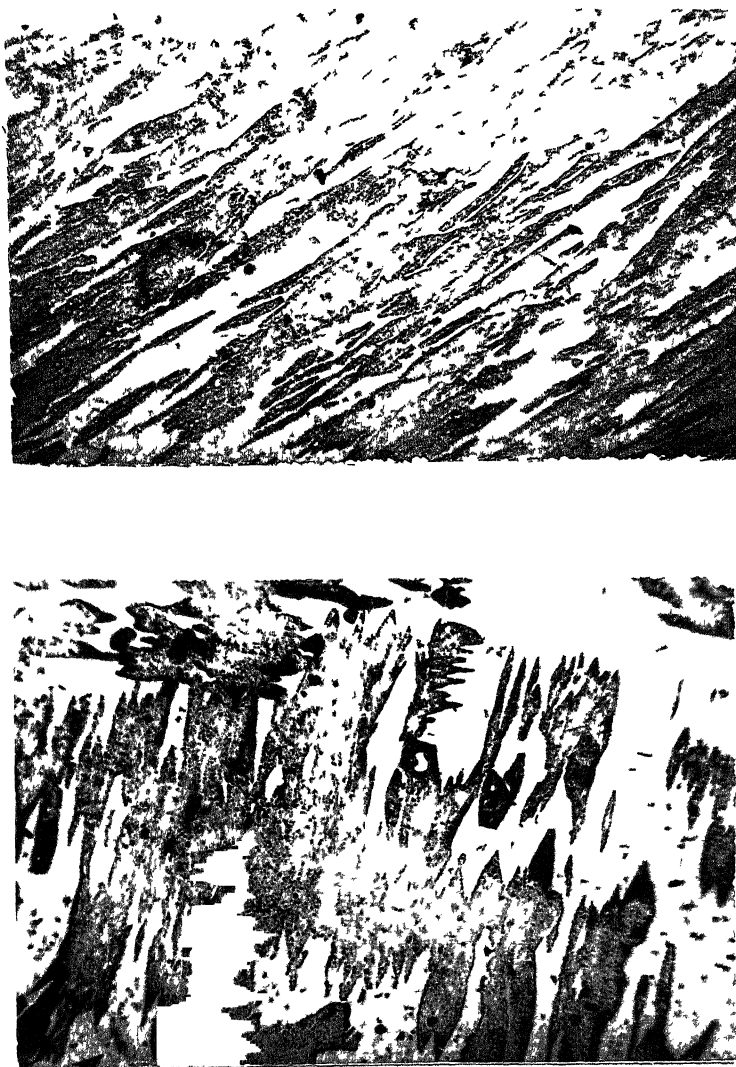


Figure 5.3. Directionally solidified Bi-35 wt% Mn alloy.

- (a) Longitudinal section-showing orientation of BiMn flakes parallel to the heat flow direction.
- (b) Transverse section-revealing cross section of BiMn flakes

Magnification x 50

Sample Calculation

Let us take the composition Bi-0.5 wt% Mn in as cast condition.

Hence, $4\pi M_S = 0.51 \text{ e.m.u./gm.}$

$$\text{or } M_S = \frac{0.51}{4\pi} \text{ e.m.u./gm.}$$

Density of this sample = 9.788 gm/cm^3

Since the applied field H is in unit of KOe., so unit of M_S has to be changed from e.m.u./gm. unit to K.Gauss. to get the dimensionless value of K and μ .

The conversion factor for the magnetometer used here in which Ni has been used as a standard sample for calibration is

$$\text{K.G. (of sample)} = (\text{e.m.u./gm.})_{\text{sample}} \times (\text{density})_{\text{sample}} \times .0122$$

The value of M_S in K.Gauss unit will be

$$M_S = \left(\frac{.51}{4\pi} \right) \times 9.788 \times .0122 \text{ K.Gauss}$$

$$\text{Therefore, susceptibility, } K = \frac{M_S}{H} = \frac{.51 \times 9.788 \times .0122}{4\pi \times 10.5}$$

$$= 0.0004617$$

$$(\because H = 10.5 \text{ KOe})$$

And,

$$\text{Permeability, } \mu = 1 + 4 \pi K$$

$$= 1 + \frac{.51 \times 9.788 \times .0122}{4 \pi \times 10.5} \times 4 \pi$$

$$= 1.0057994$$

* Note :

Density varies from 9.788 gm./cm³ to 8.9705 gm./cm³ in the composition range from 0.5 wt% Mn to 35 wt% Mn in the Bi-Mn alloys.

TABLE I

SOME MAGNETIC PROPERTIES OF THE DIRECTIONALLY
SOLIDIFIED AND AS CAST Bi-Mn ALLOYS

Sl. No.	Composition	Condition	$4\pi M_s$ at 10.5 Koe emu/gm	$4\pi M_r$ emu/gm	H_c oe	K at 10.5 Koe	μ_{max}
1	2	3	4	5	6	7	8
1	Bi-0.5 wt%Mn	As cast	0.51	0.045	50	0.0004617	1.0057994
2	-do-	D.S. longitudinal	0.49	0.075	50	0.0004441	1.005578
3	-do-	D.S. Transverse	0.48	0.03	50	0.0004345	1.0054582
4	Bi-2 wt% Mn	As cast	3.74	0.85	750	0.0033738	1.042376
5	-do-	D.S. longitudinal	1.00	0.83	5800	0.0009021	1.0113304
6	-do-	D.S. Transverse	0.61	0.11	520	0.0005502	1.0069115
7	Bi-3 wt% Mn	As cast	10.7	0.51	140	0.009513	1.1194835
8	-do-	D.S. longitudinal	10.9	0.67	100	0.0096908	1.1217166
9	-do-	D.S. Transverse	8.4	0.4	80	0.0074681	1.0938
10	Bi-12 wt% Mn	As cast	15.5	0.72	50	0.0136454	1.1713857
11	-do-	D.S. longitudinal	14.2	0.80	50	0.0125009	1.1570114
12	-do-	D.S. Transverse	16.2	0.64	50	0.0142616	1.1791257

Table I (Contd...)

1	2	3	4	5	6	7	8
13.	Bi-10 wt% As Cast Mn		16.1	1.14	110	0.0141355	1.1775428
14	-do- D.S. Longitudinal		15.4	0.75	110	0.0135213	1.1698285
15	-do- D.S. Transverse		19.8	1.1	100	0.0173839	1.2183428
16	Bi-15 wt% As cast Mn		17.2	1.24	100	0.0150265	1.1887333
17	-do- D.S. Longitudinal		15.3	1.165	180	0.0133666	1.1678857
18	-do- D.S. Transverse		13.1	0.9	160	0.0114444	1.1437428
19	Bi-30 wt% As cast Mn		17.3	0.725	100	0.014546	1.182698
20	-do- D.S. longitudinal		15.0	0.965	120	0.0126122	1.1584095
21	-do- D.S. Transverse		12.4	0.68	110	0.0104261	1.1309523
22	Bi-35 wt% As cast Mn		17.5	1.21	120	0.0145222	1.1824
23	-do- D.S. longitudinal		13.0	1.155	200	0.0107901	1.1355238
24	-do- D.S. Transverse		11.8	0.81	180	0.0097922	1.1229904

D.S. = Directionally Solidified

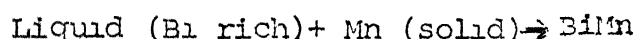
TABLE II

A COMPARISON OF MAGNETIC PROPERTIES OF Bi-2wt%Mn ALLOY
WITH SOME COMMERCIAL PERMANENT MAGNETS

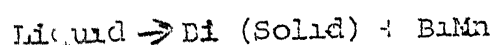
Sl.No.	Name of the alloy	H _C Oe	M _r (Gauss)
1	Bi-2wt% Mn D.S. longitudinal	5800	500
2	Co 0.Fe ₂ O ₃ Cobalt ferrite	400-600	3000-5000
3	Alnico-5	600	12,500
4	Carbon steel 0.9C, 1.0 wt% Mn	50	10,000
5	MnBi 21 wt% Mn+79 wt% Bi	3,650	-

D.S. = Directionally Solidified

Microstructures of directionally solidified Bi-Mn binary alloys are shown in (Figure 5-1 to 5-3). These figures show that BiMn flakes are embedded in Bi - matrix or Mn-matrix parallel to the solidification direction. A binary phase diagram¹³ of Bi-Mn is shown in (Figure 5-6). There is very little solid solubility between Mn and Bi. The intermetallic compound BiMn forms through a peritectic reaction at 446°C as follows:



There is also a eutectic reaction at 264°C and 0.5 wt% Mn composition,



and at 21 wt% Mn, the structure is fully composed of BiMn phase.

The crystal structure of BiMn is hexagonal, in which Bi atoms occupy hexagonal closed pack positions and Mn atoms are arranged in octahedral holes parallel to the hexagonal axis in linear chains. The BiMn phase is ferromagnetic although the constituent elements Bi and Mn are non-magnetic i.e. diamagnetic and paramagnetic respectively. According to Bethe-Slater⁵ after alloying Mn and Bi, a long-range ordering sets in, in which the Mn-Mn interatomic distance becomes large enough for the exchange interaction to become positive (Figure 5-7)⁶. Ferromagnetism

results only when the exchange interaction is positive with the electron spins of the neighbouring atoms parallel. It has been experimentally shown that the manganese atoms are farther apart in this alloy than in pure manganese, giving rise to a positive exchange interaction.

The increase in coercivity in directionally solidified alloys in comparison to as cast structures is due to the alignment of BiMn flakes parallel to the direction of solidification (Fig. 5-2 and 5-3) lying in the basal plane of hexagonal crystal of BiMn. Due to anisotropy in BiMn crystal, the coercivity is low in the transverse direction (C-axis of BiMn crystal).

The coercivity reaches a maximum (5800 oers) comparable to hard magnetic material at 2 wt% Mn⁷, making this composition suitable to be used in memory devices. In coercivity vs composition of alloy curve (Fig. 5-5) only one peak at 2 wt% Mn (except for 21 wt% Mn which is fully ferromagnetic), composition is achieved whereas for other compositions, coercivity decreases sharply and remains more or less constant (varies from 50 oers to 200 oers) (Table 1).

All alloys having composition of Bi-0.5 wt% Mn to Bi - 12 wt % Mn exhibit good linear relationship (fig. 5-4) between saturation magnetisation (M_s) and the weight percent of the added element (Mn) in the Bi-Mn alloy. For cast alloys, saturation magnetisation (M_s) remains constant for increasing

wt % Mn from 13 wt % to 35 wt% Mn. For directionally solidified alloys (transverse section), saturation magnetisation (M_s) shows a peak at 13 wt % Mn composition and then for 15 wt % Mn composition M_s suddenly decreases and then for higher wt% Mn (upto 35 wt %) there is a small and slight decrease of M_s value. For directionally solidified (longitudinal section) alloys, there is a gradual and slight decrease of M_s value for composition from D1 - 13 wt % Mn to 35 wt % Mn (fig - 5-4).

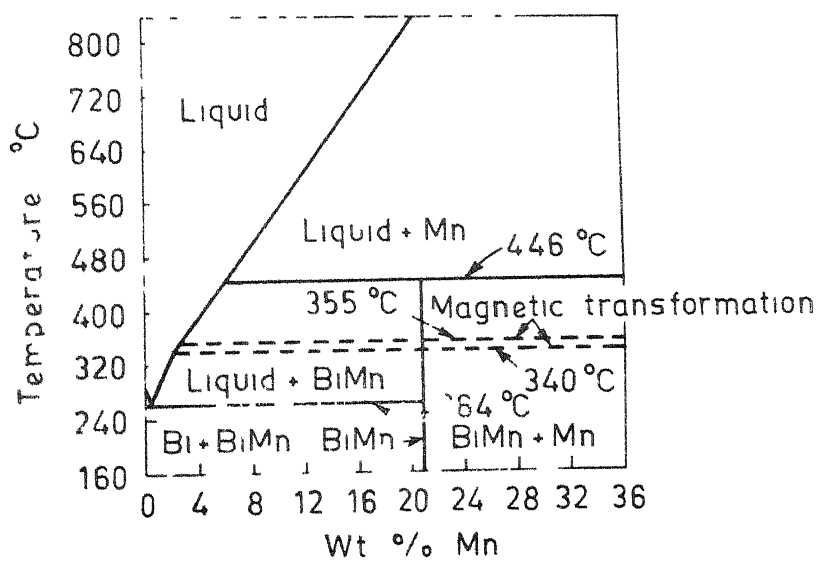


Fig 56 Phase diagram of the Bi-Mn system

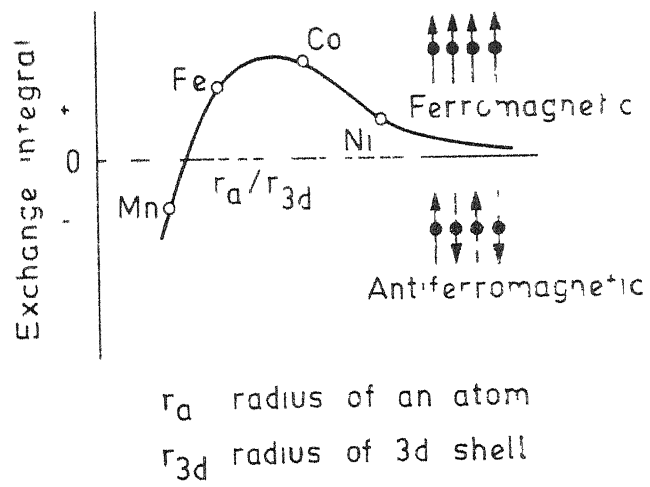


Fig 57 Bethe - Slater curve (schematic)

SUMMARY

Directionally solidified Bi-Mn alloys exhibit anisotropic magnetic properties- higher coercivity along the axis of solidification and lower coercivity transverse to the axis of solidification. Some of the magnetic properties like saturation magnetisation (M_S), remanent magnetisation (M_R) and coercivity (H_C) were measured from which susceptibility (K) and permeability (μ) is calculated (Table 1).

REFERENCES

1. J.L. Walter and H.E. Cline, Metallurgical Transactions, 1, 1970, 1226.
2. F.L. Versnyder and M.E. Shank, Materials Science and Engineering, 6, 1970, 246.
3. M.C. Flemings, 'Solidification Processing', McGraw-Hill, U.S.A., 1974.
4. C.H. Lund, 'Maximum High Temperature Properties of Ni-Rich Superalloys Based on Composition or Directional Solidification', Foundry Trade Journal, 128, 1970, 815.
5. P.R. Sahm and M.O. Speidel (Ed.), 'High-Temperature Materials in Gas Turbines', Elsevier Scientific Publishing Co., Amsterdam, 1974.
6. B.D. Culity, 'Introduction to Magnetic Materials'.
7. S.K. Nath, 'Directional Solidification and Magnetic Properties of Some Bi-Mn Alloys', M.Tech. Thesis, I.I.T. Kanpur, 1979.
8. Pol Duwez, 'Structure and Properties of Alloys Rapidly Quenched from the Liquid State', Transactions of American Society for Metals, 60, 1967, 608.
9. Chester T. Sims and Williams C. Hagel (Ed.), 'The Superalloys', Wiley-Interscience Publication, 1972, U.S.A.
10. G.J. Davies, 'Solidification and Casting', Applied Science Publishers Ltd., London, 1973.
11. A.F. Giamci and J.G. Tschinkel, 'Liquid Metal Cooling: A New Solidification Technique', Met. Trans., 7A, 1976, 1429.
12. Magnetism and Metallurgy, edited by AMI E. BERKOWITZ. and ECKART KIELLER, Volume 1.
13. A.U. Seybolt, H. Hansen, B.W. Roberts and P. Yurcisin, 'Contribution to the Bi-Mn System', Transactions of the Metallurgical Society, AIME, 206, 1956, 606-609.

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